Characterization of OCS-HCCCCH and N_2O-HCCCCH dimers: Theory and Experiment

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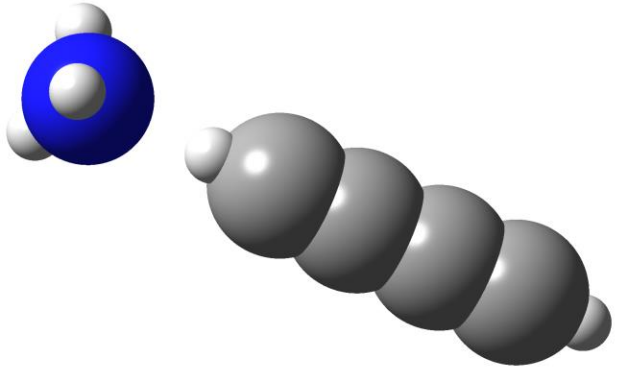
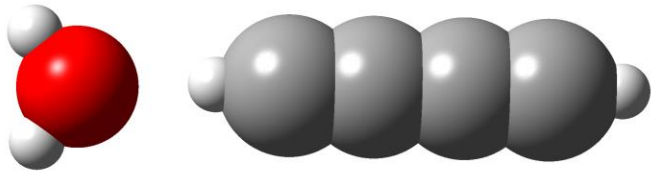
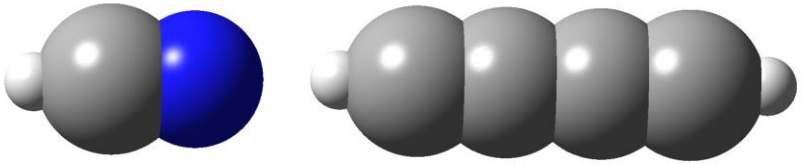
Previous Gas Phase Studies of Mixed HCCCCH Dimers

- Microwave Study: K. Matsumura, F.H. Lovas, R.D. Suenram, J. Mol. Spectrosc. 144 (1990) 123.
- NH_3-HCCCCH (C_{3v}) and H_2O-HCCCCH (C_{2v}) dimers

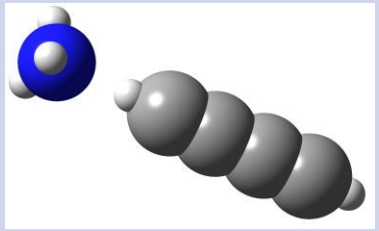
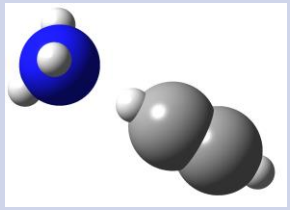
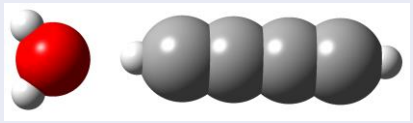
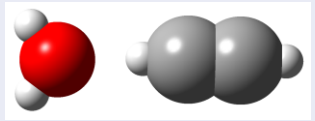
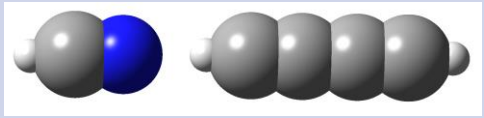
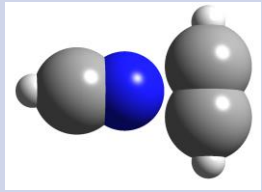
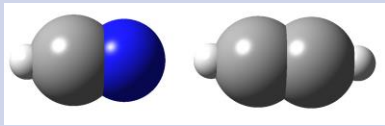




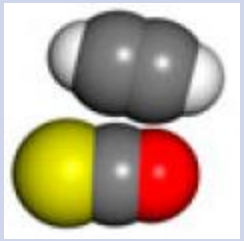
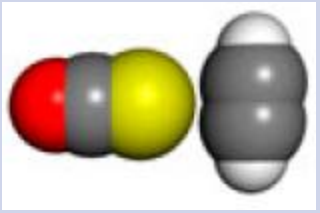
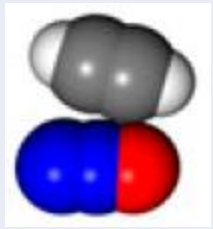
- Infrared Study: X. Yang, R.Z. Pearson, K.K. Lehmann, G. Scoles, J. Chem. Phys. 105 (1996) 10725.
- HCN-HCCCCH ($C_{\infty v}$) dimer



Structure Similarities of HCCCCH and HCCH

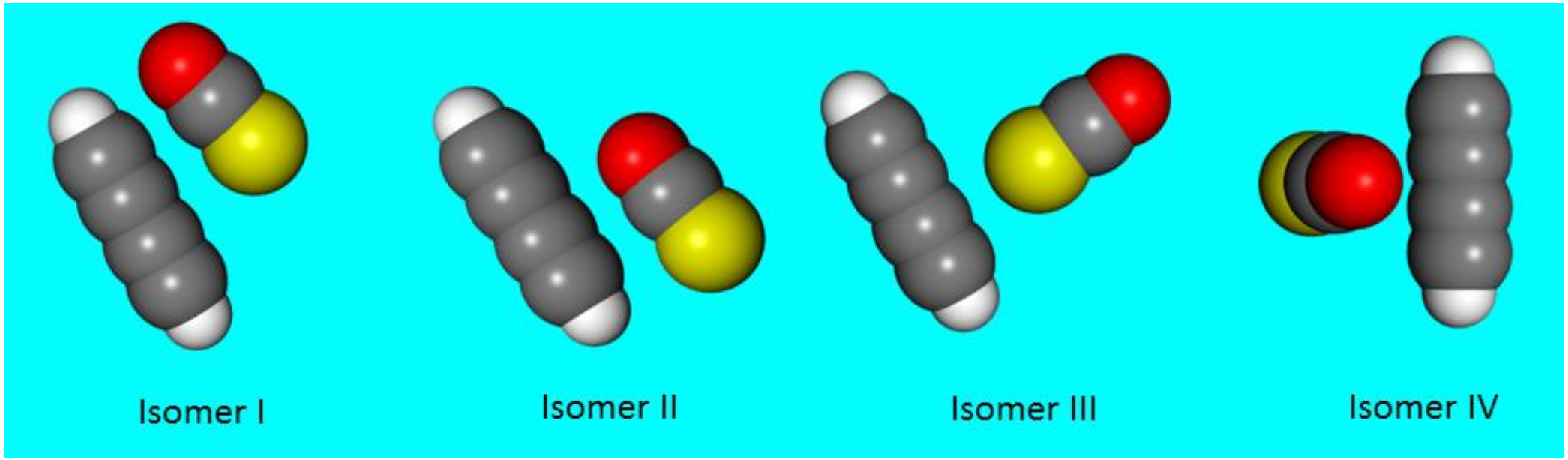
	HCCCCH		HCCH	
NH_3		Symmetric top C_{3v}		Symmetric top C_{3v} G. T. Fraser, et al. J. Chem Phys. 80 (1984) 1423
H_2O		Asymmetric top C_{2v}		Asymmetric top C_{2v} K. I. Peterson, et al. J. Chem Phys. 81 (1984) 3842.
HCN		Linear $C_{\infty v}$	 	Asymmetric top C_{2v} Linear $C_{\infty v}$ P. D. Aldrich, et al. J. Chem. Phys. 78 (1983) 3521.

OCS-HCCH and N_2O-HCCH Dimer

	HCCCCH		HCCH	
OCS	--	--		Asymmetric top C_s symmetry "S in"
				Asymmetric top C_{2v} symmetry "T-shape"
N_2O	--	--		Asymmetric top C_s symmetry "N in"

N. Moazzen-Ahmadi, A.R.W. McKellar. Int. Rev. Phys. Chem. 32 (2013) 611.

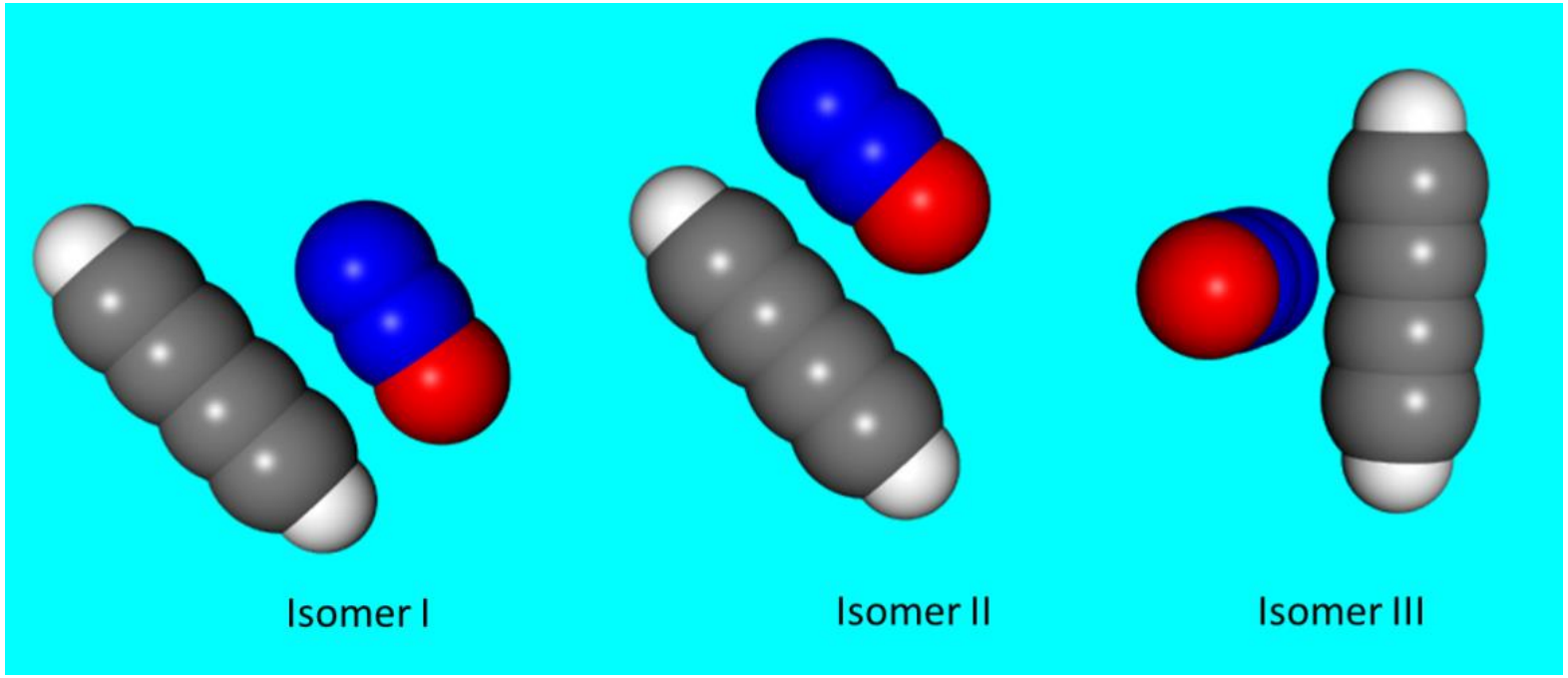
Quantum-Chemical Calculations for OCS-HCCCCH



(S-in) (O-in) T-shaped Cross-shaped

- Optimized geometries obtained with B2PLYP-D3 in conjunction with maug-cc-pvtz
- Four stationary points found corresponding to true minima on PES

Quantum-Chemical Calculations for N_2O-HCCCCH



(N-in) (O-in) Cross-shaped

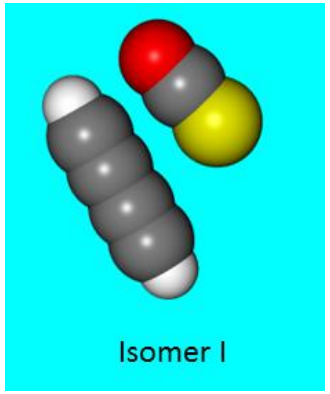
- Optimized geometries obtained with B2PLYP-D3 in conjunction with maug-cc-pvtz
- Three stationary points found corresponding to true minima on PES

Theoretical Molecular Parameters and Binding Energies of OCS-HCCCCH and N_2O-HCCCCH

	OCS-HCCCCH				N_2O-HCCCCH		
	Isomer I (S-in)	Isomer II (O-in)	Isomer III T-shaped	Isomer IV Cross-shaped	Isomer I (N-in)	Isomer II (O-in)	Isomer III Cross-shaped
A /MHz[a]	2897	4088	4255	2629	4461	4401	3262
B /MHz[a]	1277	1000	795	1243	1446	1470	1754
C /MHz[a]	886	803	670	1139	1092	1102	1394
$BE_{(CP)}$ /cm^{-1} [a]	-776	-630	-584	-668	-727	-675	-612
$BE_{(CBS+CV+ZPV)}$ /cm^{-1} [b]	-479	-252	-332	-384	-472	-227	-371

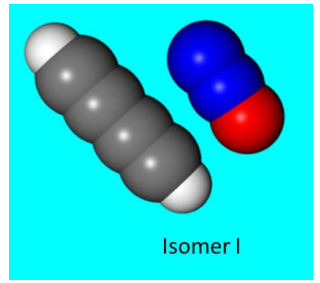
- [a]Optimized geometries and binding energy obtained with B2PLYP-D3 in conjunction with maug-cc-pvtz
- [b]Binding energy obtained from extrapolated energies to the CBS limit at CCSD(T) level of theory corrected by CV effects.

Further Calculations on the Lowest Energy Isomers of OCS-HCCCCH and N_2O-HCCCCH



	OCS-HCCCCH		N_2O-HCCCCH	
	Isomer I		Isomer I	
	CCSD(T)[a]	CCSD(T*)-F12c[b]	CCSD(T)[a]	CCSD(T*)-F12c[b]
A	2856	2897	4487	4540
B	1205	1274	1395	1446
C	847	885	1064	1097

units in MHz



- [a]Optimized geometries obtained at CCSD(T,fc) level of theory in conjunction with cc-pVTZ basis set.
- [b]Optimized geometries obtained at CCSD(T*)-F12c level of theory in conjunction with VTZ-F12 basis set.

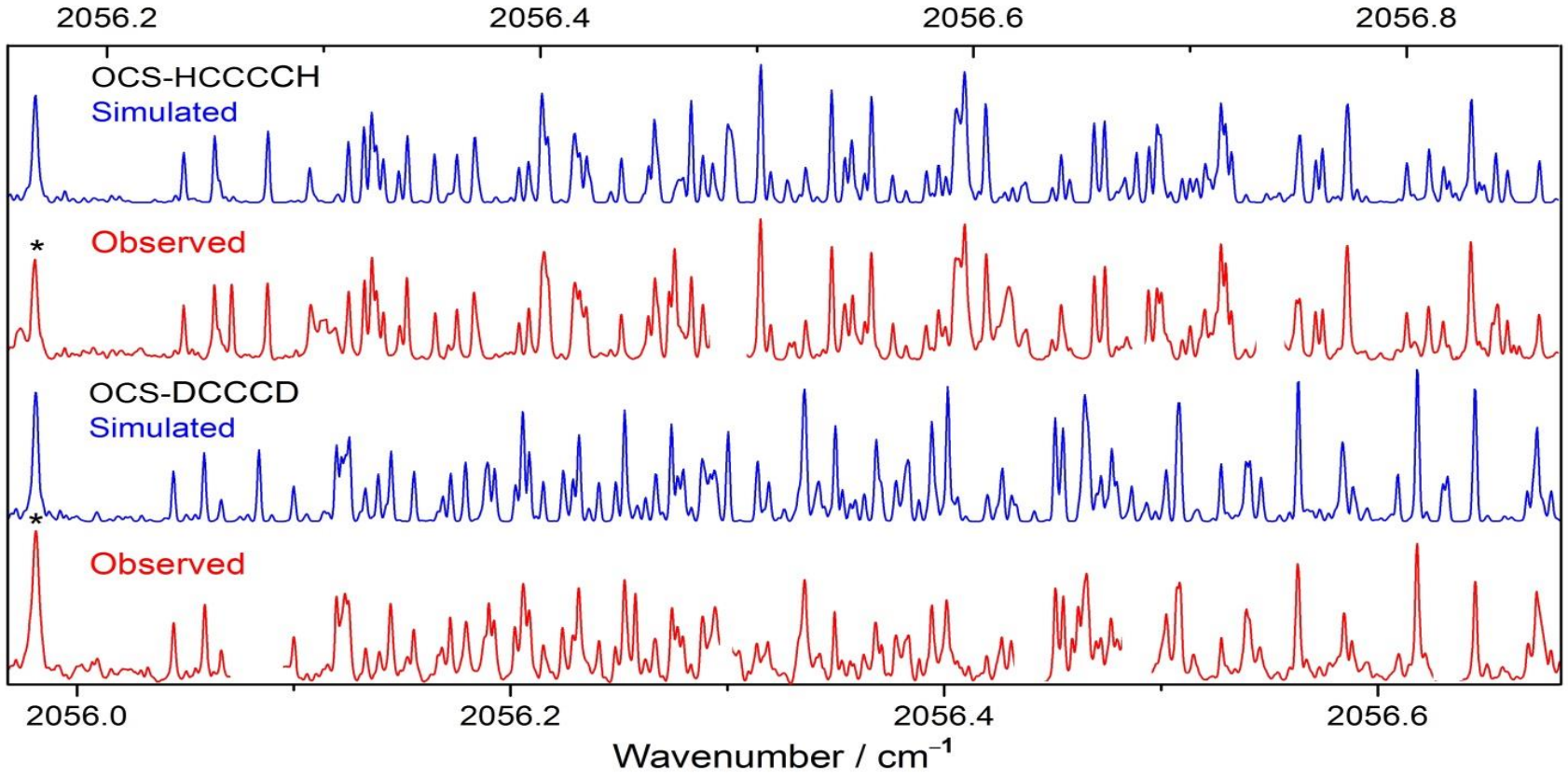
Experimental Conditions

- Pulsed supersonic slit jet apparatus
- Tuneable Diode Laser (OCS ν_1 fundamental ~2050cm^{-1})
- Daylight Solutions quantum cascade laser (N_2O ν_1 fundamental ~2220 cm^{-1})

- <u>Expansion Mixture</u>:
  0.1 % OCS or N_2O
  0.3 % HCCCCH or DCCCCD
  Helium carrier gas
  8 atm backing pressure

- <u>Frequency calibration</u>:
  OCS or N_2O reference
  Etalon (fsr = 0.009976 cm^{-1})
  PGOPHER

Observation of OCS-HCCCCH and OCS-DCCCCD



a/b asymmetric top hybrid band
a:b transition moment ratio = 1:3

245 transitions assigned for OCS-HCCCCH
159 transitions assigned for OCS-DCCCCD

T_{rot} = 2.5 K

Line width = 0.0018 cm^{-1}

Experimental Molecular Parameters for OCS-HCCCCH

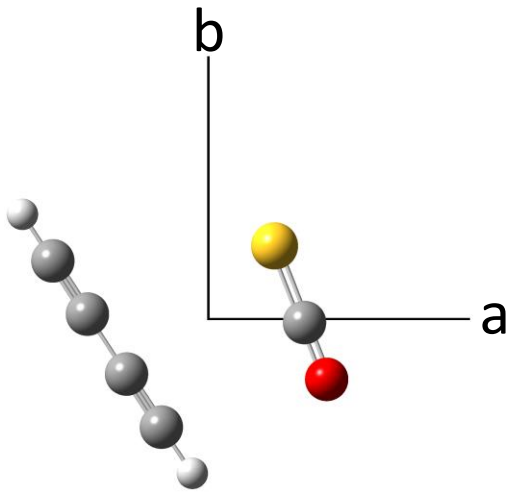
	OCS – HCCCCH	**OCS – DCCCCD**
ν_0 / cm^{-1}	2056.16809(3)	2055.98241(5)
A' / MHz	2891.907(68)	2692.82(28)
B' / MHz	1242.930(34)	1205.53(12)
C' / MHz	867.841(16)	831.664(79)
D_K' / kHz	6.3(22)	
D_{JK}' /kHz	5.7(19)	15.6(24)
A'' / MHz	2892.78(15)	2693.92(28)
B'' / MHz	1244.416(74)	1206.46(12)
C'' / MHz	869.008(55)	832.221(83)
D_K'' / kHz	6.3(22)	
D_{JK}'' / kHz	5.7(19)	12.8(24)
Δ / a.m.u Å^2	0.78	0.77

Inertial defect

$$\Delta = I_c - I_a - I_b$$

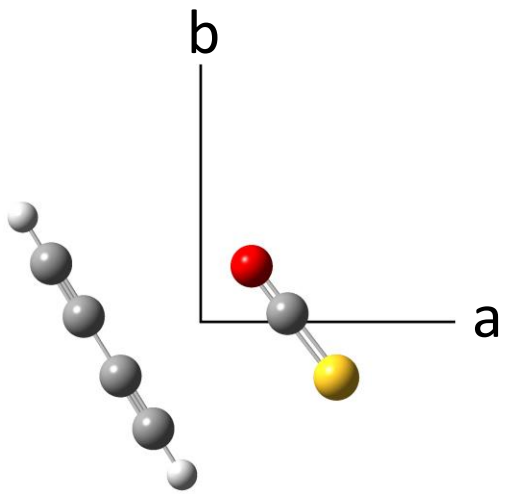
$\Delta \sim 0 \quad \rightarrow planar\ geometry$

Expected Asymmetric Top Band Types



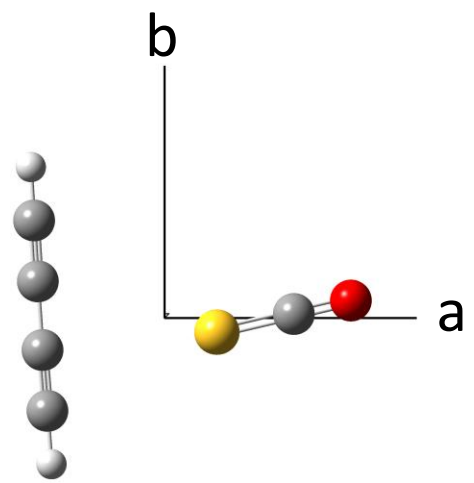
Isomer 1 (S-in)

a/b hybrid
a:b = 1:3



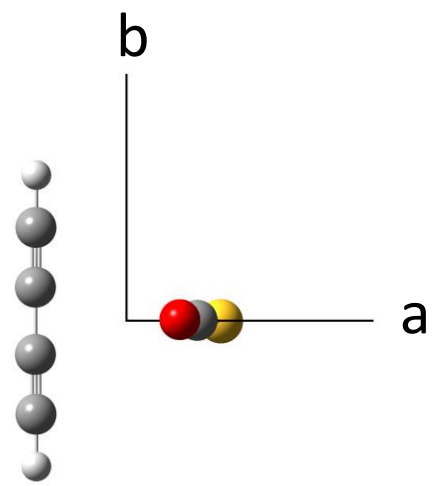
Isomer 2 (O-in)

a/b hybrid
a:b = 1:1



Isomer 3 T-shaped

Mostly a type



Isomer 4 Cross-shaped

Mostly c type

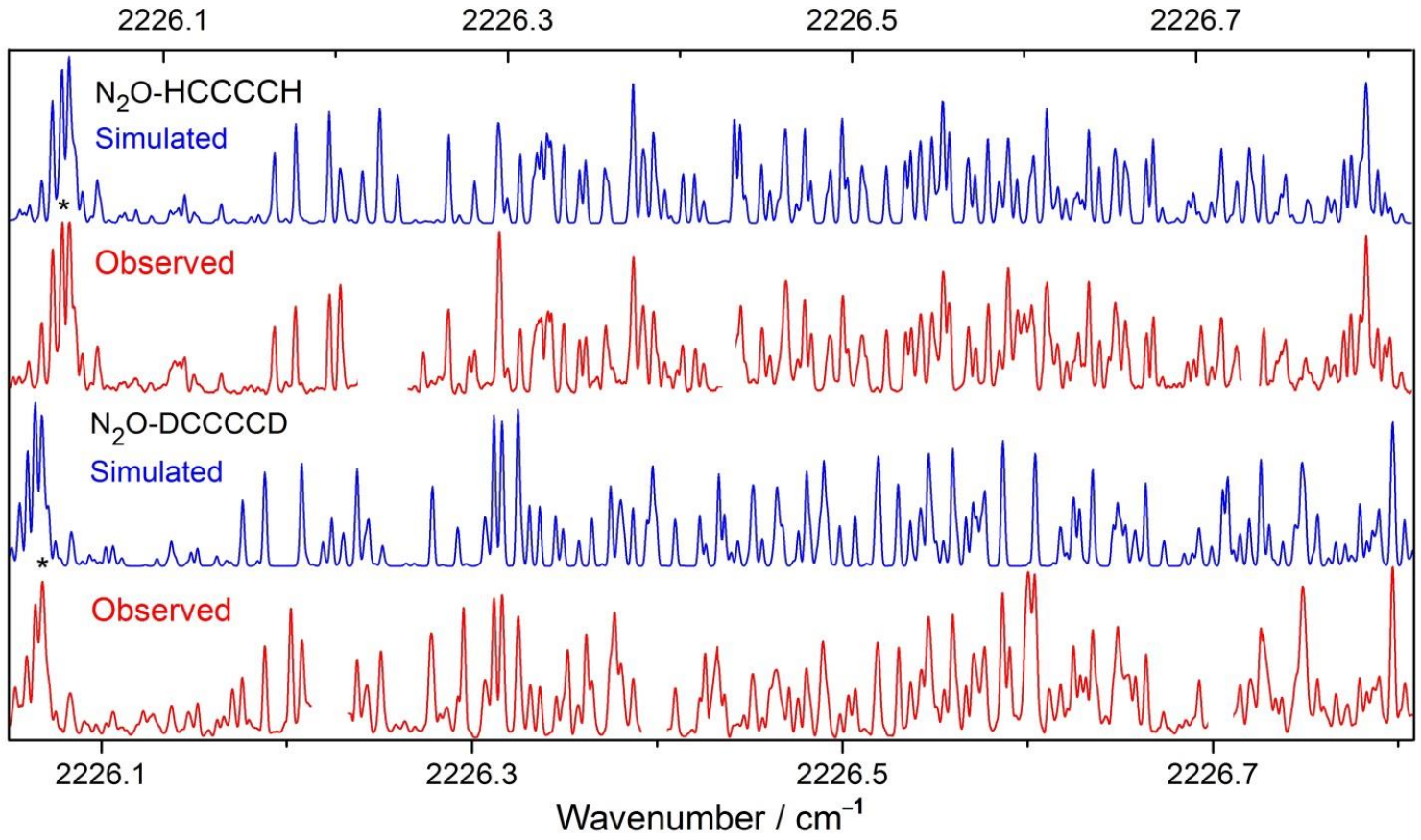
- Expected band type when exciting the ν_1 (CO stretch) vibration of OCS

Theory and Experiment Molecular Parameters of OCS –HCCCCH and OCS-DCCCCD

	Experiment		CCSD(T*)-F12c	
	OCS – HCCCCH	OCS – DCCCCD	OCS – HCCCCH Isomer 1	OCS – DCCCCD Isomer 1
ν_0/ cm^{-1}	2056.16809(3)	2055.98241(5)		
A' / MHz	2891.907(68)	2692.82(28)		
B' / MHz	1242.930(34)	1205.53(12)		
C' / MHz	867.841(16)	831.664(79)		
D_K' / kHz	6.3(22)			
D_{JK}' / kHz	5.7(19)	15.6(24)		
A" / MHz	2892.78(15)	2693.92(28)	2882.07	2684.26
B" / MHz	1244.416(74)	1206.46(12)	1261.10	1223.09
C" / MHz	869.008(55)	832.221(83)	876.38	839.43
D_K" / kHz	6.3(22)			
D_{JK}" / kHz	5.7(19)	12.8(24)		
Δ / a.m.u Å^2	0.78	0.77		

Equilibrium rotational constants at CCSD(T*)-F12c/VTZ-F12 level of theory augmented by vibrational corrections computed at B3LYP-D3 level.

Observation of N_2O-HCCCCH and N_2O-DCCCCD



T_{rot} = 2.5 K
Line width = 0.0022 cm^{-1}

a/b asymmetric top hybrid band
a:b transition moment ratio = 2:3

166 transitions assigned for N_2O-HCCCCH
121 transitions assigned for N_2O-DCCCCD

Experimental Molecular Parameters of N_2O-HCCCCH

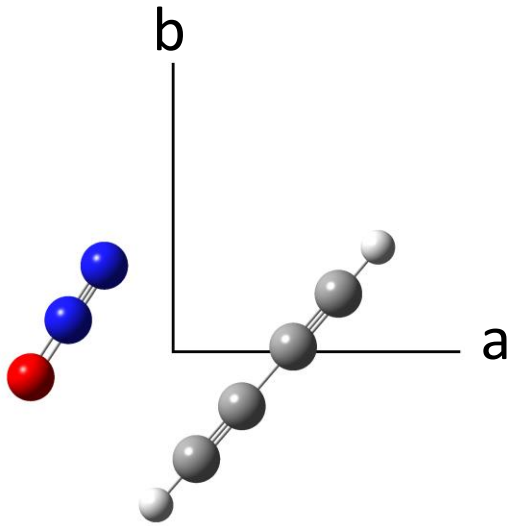
	N_2O – HCCCCH	N_2O – DCCCCD
ν_0 / cm^{-1}	2226.05079(5)	2226.07274(5)
A' / MHz	4479.78(35)	4117.27(20)
B' / MHz	1409.16(12)	1358.51(12)
C' / MHz	1069.838(81)	1019.606(90)
D_K' / kHz	82.9(77)	
D_{JK}' / kHz	-12.2(25)	
A'' / MHz	4498.57(28)	4134.60(52)
B'' / MHz	1409.03(12)	1358.33(12)
C'' / MHz	1070.783(76)	1020.552(99)
D_K'' / kHz	91.8(51)	93(28)
Δ / a.m.u Å^2	0.96	0.91

Inertial defect

$$\Delta = I_c - I_a - I_b$$

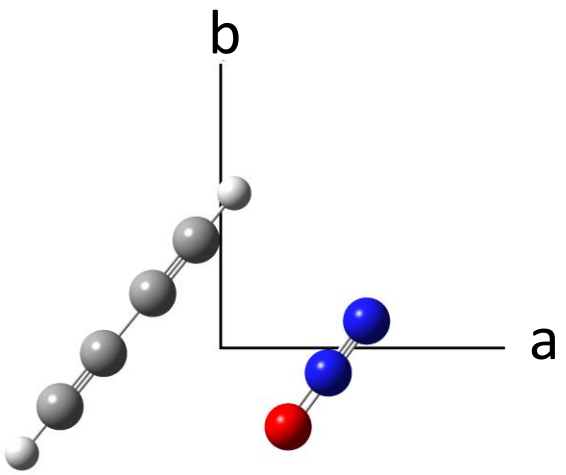
$\Delta \sim 0 \quad \rightarrow planar\ geometry$

Expected Asymmetric Top Band Types



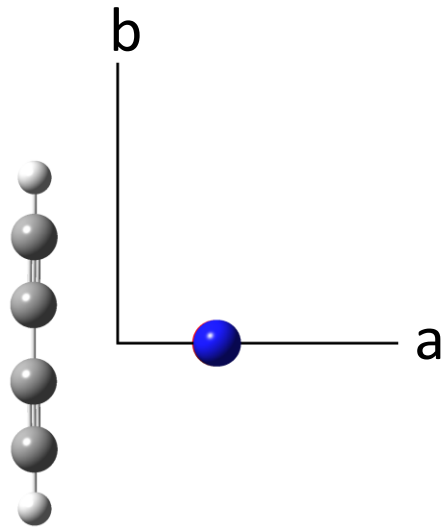
Isomer 1 (N-in)

a/b hybrid
a:b = 2:3



Isomer 2 (O-in)

a/b hybrid
a:b = 1:1.3



Isomer 3 Cross-shaped

c type

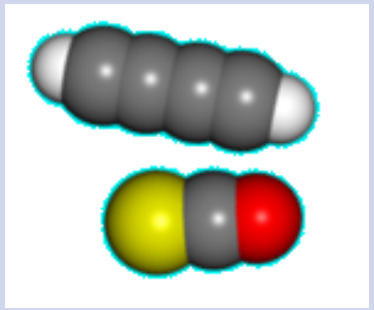
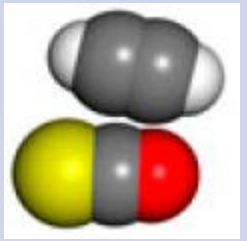
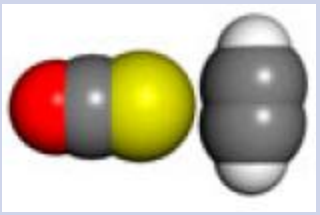
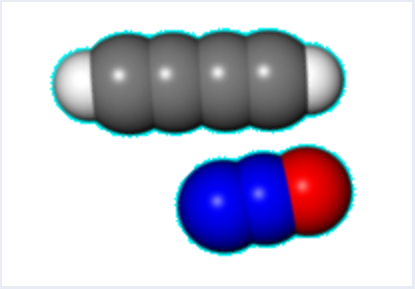
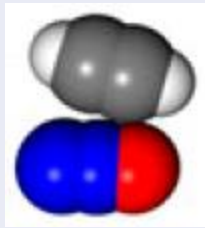
- Expected band type when exciting the ν_1 (N-N stretch) vibration of N_2O

Theory and Experiment Molecular parameters of N_2O-HCCCCH and N_2O-DCCCCD

	Experiment		CCSD(T*)-F12c	
	N_2O – HCCCCH	N_2O – DCCCCD	N_2O – HCCCCH Isomer 1	N_2O – DCCCCD Isomer 1
ν_0 / cm^{-1}	2226.05079(5)	2226.07274(5)		
A' / MHz	4479.78(35)	4117.27(20)		
B' / MHz	1409.16(12)	1358.51(12)		
C' / MHz	1069.838(81)	1019.606(90)		
D_K' / kHz	82.9(77)			
D_{JK}' / kHz	-12.2(25)			
A" / MHz	4498.57(28)	4134.60(52)	4485.29	4117.35
B" / MHz	1409.03(12)	1358.33(12)	1434.99	1384.70
C" / MHz	1070.783(76)	1020.552(99)	1085.21	1034.36
D_K" / kHz	91.8(51)	93(28)		
Δ / a.m.u $Å^2$	0.96	0.91		

Equilibrium rotational constants at CCSD(T*)-F12c/VTZ-F12 level of theory augmented by vibrational corrections computed at B3LYP-D3 level.

OCS-HCCCCH and N_2O-HCCCCH Dimer compared with OCS-HCCH and N_2O-HCCH Dimer

	HCCCCH		HCCH	
OCS		--	 	Asymmetric top C_s symmetry "S in" Asymmetric top C_{2v} symmetry "T-shape"
N_2O		--		Asymmetric top C_s symmetry "O in"

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